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Improvements in wettability of silver copper eutectic alloys by additions of alkali and alkali-earth metals

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C E Donaldson

IMPROVEMENTS IN WETTABILITY OF
SILVER COPPER EUTECTIC ALLOYS...

Thesis
D6437

Project Report

Course GE-655

Improvements in the Wettability of Silver Copper Eutectic Alloys
by Additions of Alkali and Alkali-Earth Metals.

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20 May 1964.

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Introduction. Brazing is a process whereby metal parts are joined by a filler metal or alloy whose melting point is above 800°F, (as distinguished from soldering) but lower than that of the parts to be joined. Since melting of the joined parts does not occur, it is almost intuitively obvious that the filler metal must "wet" the parts for proper joining. Like so many other areas of metallurgy, there is much empirical and semi-empirical data on the subject of brazing, and a substantially complete theory exists, but the actual measurement of some vital parameters is not yet possible, nor do explanations exist for all observed departures from theoretical behavior. It is against this background that the art and science of brazing is practiced today.

The work of Bredas, Canonico and Schwartzbart (1), (2), (3), (4), (5) on improvement in wettability of silver brazing alloys by additions of lithium suggested that similar results ought to be observed with additions of other alkali and alkali-earth metals. Although these authors investigated certain of these other additive metals, it was felt that their investigation left some unanswered questions including mechanism, and a general thermodynamic rationale for their results.

The intent of the present experiment was to summarize a coherent, theoretical treatment of the field of brazing, with special emphasis on the effects of additions of small amounts of the energetic Groups I-A and II-A elements to standard brazing alloys. Additionally, a minimum amount of laboratory work involving preparation of and simple brazing with some of these alloys was planned within existing time and fund limitations.

General Theory. When two pieces of solid metal are joined by brazing, the liquid filler, or "braz", metal must flow between the two surfaces to be joined, ideally filling the entire overlap space between the two metal parts. The filler must, in addition, adhere to the parts so as to develop "joint strength". The process whereby the filler metal flows between the parts is capillarity and the process whereby it adheres to the parts is a function of solid solubilities (6)(7), i.e., of the "Work of Adhesion", W_A .

Capillary flow takes place because of a pressure difference which arises under the liquid meniscus as a function of orthogonal, general radii of curvature, R_1 and R_2 . This pressure difference, which is generically related to a chemical potential difference, may be expressed in an equation due to Laplace:

$$\Delta P = -\gamma \left[\frac{1}{R_1} + \frac{1}{R_2} \right] = -\gamma (K_1 + K_2) \text{ where } \Delta P \text{ is the pressure difference, } \gamma \text{ the interfacial tension between liquid and solid, and } K \text{ is curvature.}$$

In essence, this equation says that whenever there is a curved interface between two entities, there will exist a pressure difference which will tend to move the boundary toward the center of curvature. This equation is rigorously derived by Adam (3). For closely spaced flat plates, D cm apart, which would simulate a simple configuration for two pieces to be joined by brazing, the radius of curvature along the line where liquid joins solid is infinite so that $1/R_1 = 0$, or $K_1 = 0$. For the meniscus itself, the curvature is $K_2 = (D/2) \cos \theta$, where θ is the angle of contact between the edge of the meniscus and the solid surface, as in figure (1). For perfect wetting, $\theta = 0^\circ$

and $\Delta P = -2/D$. (For concentric cylinders, e.g., a pipe or tube in a pipe coupling, $K_1 \neq 0$ and the expression for pressure must include both the curvature of and along the meniscus.)

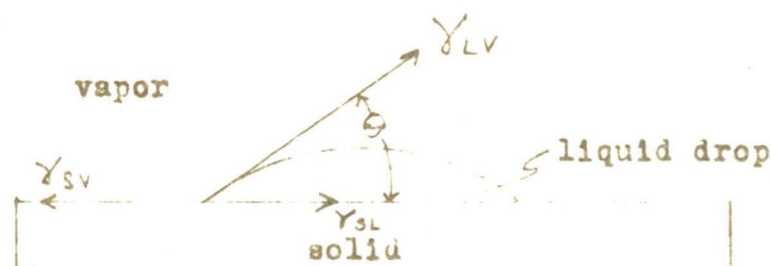


Figure (1). Vector diagram of surface tension forces acting at the rim of a liquid drop.

The contact angle, θ , at a liquid-solid interface is directly related to the ability of the liquid to wet the solid. It is seen that for static force equilibrium to obtain, $\gamma_{sv} = \gamma_{lv} \cos \theta + \gamma_{sl}$. At the extremes, if $\theta = 180^\circ$, the liquid will rest as a spheroidal globule on the solid surface. In a field-free environment, it would contact the solid in a point and would not spread on it. If $\theta = 0^\circ$, then $\gamma_{sv} = \gamma_{lv} + \gamma_{sl}$, and the liquid would spread over the solid surface, continuing to spread until some other force caused it to stop. Thus, it would wet the surface.

From the above, it is seen that the actual interfacial tensions of the phases actually in contact all have a prime effect on the wettability of a solid by a liquid. It is the many ways in which these parameters can be altered by unknown or unsuspected substances and effects in practice that renders the precise mathematical prediction of brazing performance so difficult.

Udin, Funk and Wulff (9) develop an equation describing

the effects of both dilatation and constriction of the flow path upon the capillary flow velocity of a brazing filler metal. Between two flat plates separated by a distance D , as in figure (2), note that the flow direction is toward the direction of the cen-

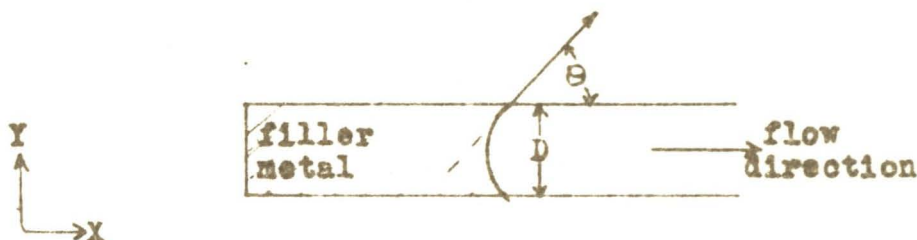


Figure (2). Flow configuration between flat plates.

ter of curvature of the interface. This curved meniscus is a direct function of the liquid and solid surface free energies (or surface tensions) and the solid-liquid interfacial tension, γ_{sl} . Thus the pressure difference tending to drive the liquid into the space between the plates is $\Delta P = \frac{-2\gamma \cos \theta}{D}$. Assuming laminar flow, and a liquid viscosity, μ , the interface will advance a distance $x = \sqrt{(\gamma D)/(3\mu)} t$ in time t . For a flow path with a dilatation configured as in figure (3), it is shown that

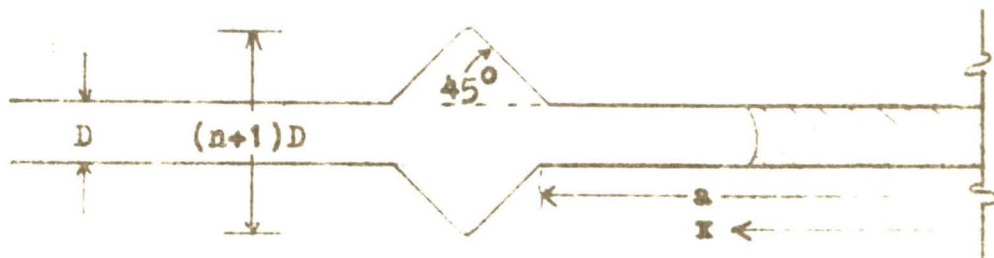


Figure (3). A dilated capillary dam.

the time to fill from the start of the joint past the dam is

$$t = \frac{6\mu an}{\gamma} \left[1 + n/2 \right] + \frac{3\mu a^2}{\gamma D} .$$

The dilatation could be a gouge or tool mark perpendicular to the direction of flow.

The converse type of capillary dam is the constriction, as shown in figure (4). Here the effect is the familiar hydraulic

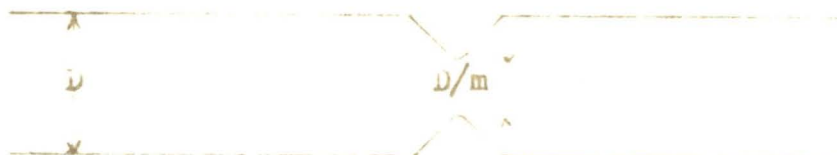


Figure (4). A constricted capillary dam.

effect of an orifice where m is a measure of the degree of constriction, as shown, and the dam effectively increases the flow path length by a factor of $\frac{m^2 - 1}{2}$ D . For practical dimensions, suffice it to say that in a prepared brazing joint of nominal 0.005 in. clearance, a few constrictions to 0.001 in. would not seriously increase the flow time, but "wringing" constrictions of, say, 0.0001 in. would for all practical purposes stop the flow of braze filler metal, resulting in an incompletely filled joint.

It has long been standard brazing practice to use a metal halide or borate as a flux. These salts act as oxide solvents and serve to clean the surface of the work and keep it that way during the heating period. The flux also protects the heated work surface in the vicinity of the brazing area from oxidation. Oxide saturation of and oxygen diffusion through the flux rather soon render it useless in further protecting the work. Bredzs' "Rotation Phenomenon" (2) vividly portrays the limited period of

protection afforded by the usual thin film of flux used in brazing practice. The end of protection is marked by the onset of dewetting of the brazed surfaces. Thus, the joint cannot be held indefinitely "at heat" during brazing lest it deteriorate, and it is definitely advantageous to secure high rates of filler metal flow so that the joint may be quickly "made" and cooled.

Udin, Funk and Wulff (10) develop an analysis of the effects of flux on the flow characteristics of the filler metal. Contrary to popular belief, the flux does not appreciably affect the surface tension of the filler metal because it is generally insoluble in it. Its effect on velocity of flow of filler metal is primarily due to its viscosity and the fact that the filler metal, in filling the flow space, must displace the molten flux. Thus, the primary benefits of the flux are surface cleaning and protection. Its function is not unlike that of a slag in metal production.

Markins (11) has, by thermodynamic reasoning, developed a simple criterion for the spreading of a liquid on another surface. His "spreading coefficient", S , is the decrease in Gibbs' Free Energy, $-\Delta G$, which occurs when the liquid spreads. Thus the condition for spreading is that S be positive (i.e., $\Delta G < 0$). If a drop of liquid B placed on the surface of A tends to spread, then $S = \gamma_a - (\gamma_b + \gamma_{ab})$ where γ_{ab} is the interfacial tension between the two phases. An equation due to Dupre' for the work of adhesion between two substances is $w_A = \gamma_a + \gamma_b - \gamma_{ab}$. The work of cohesion of a substance is $w_C = 2\gamma_b$. Thus, $S = w_A - w_C$ and spreading of a liquid on another surface will occur if the

work of adhesion between the two is greater than the cohesive work of the liquid. Bondi (12) develops the complete thermodynamic argument. He further, by some simplifying assumptions, arrives at the very useful necessary (but insufficient) condition for spreading of a liquid on a solid: $\gamma_s > \gamma_l$.

It has been experimentally observed that in most cases, thin layers - sometimes even monomolecular layers - of oxides and sulfides, and organic substances (oils, greases, dirt, etc.) reduce the apparent surface tension, γ_s , of essentially all metals drastically. Reported reductions of γ_s by a factor of two by minute amounts of foreign matter are not uncommon. Such reductions in γ_s reduce the wettability of solid metal by liquid filler metal, often to the point where no spreading will take place. Hence the need for extreme cleanliness of the work, a point that is drilled into the mind of every apprentice brazer. Conversely, any addition tending to lower the γ_l of the liquid filler alloy will improve spreading.

Evidently the effects of some alkali and alkali-earth metals in improving the spreading ability of certain brazing alloys can be ascribed to either their extreme chemical reactivity wherein they raise γ_s by reducing the base (work) metal oxide film, or to their solubility in the filler metal and subsequent reduction of its surface tension, γ_l . Probably both effects are manifested to a degree. The remarkable improvement of spreading ability of molten silver on steel, etc., due to small (0.1% - 1.0%) additions of lithium or barium reported by Bredas (2) imply that the additive must be positively adsorbed in the filler metal surface. Accord-

ing to the Gibbs adsorption equation, $\frac{\partial \gamma_1}{\partial c_2} = -\frac{\Gamma_2 RT}{c_2}$, where γ_1 is the filler metal surface tension, c_2 is the molar concentration of additive (i.e., Li or Ba), Γ_2 is the surface excess concentration of the additive, R is the universal gas constant and T the absolute temperature, °K. Then, when Γ_2 is positive, that is, when there is a tendency for the additive metal to be concentrated in the surface layer of the molten filler metal, $\frac{\partial \gamma_1}{\partial c_2}$ is seen to be negative. Obviously this leads to an improvement in the spreading ability of the filler alloy. This phenomenon requires, of course, that the additive metal be soluble in the filler metal.

If, in addition to the above effect, the additive metal should reduce the oxide layer present on the base metal surface, the effective surface tension of the base metal, γ_s , would be raised. For this reaction to occur, there must be a net negative Gibbs free energy of reaction when the activity of the additive metal is considered. The effect of a high surface excess concentration Γ_2 of additive metal would be to increase its activity at the filler metal - base metal interface. For the highly reactive Groups I-A and II-A metals, this practically insures their ability to reduce, for example, FeO, CuO, or NiO, to mention a few of the more commonplace base metal oxides, even when they are present in very small concentrations. This problem is discussed further by Bredas and Schwartzbart (13). However, the effect is short-lived because the small concentrations of active additive will be quickly consumed if there is a thick surface layer of base metal oxide to be reduced, or indeed if the

molten filler metal alloy is long exposed to the atmospheric oxygen.

Bredas and Schwartzbart (14) have developed an analysis of the surface activity of lithium in silver - lithium brazing alloys wherein they purport to use the absolute values of surface energies reported in the literature. While their results appear to be qualitatively correct, the question arises: were the results correct because of the degree of accuracy to which the physical parameters used were known, or because the exact thermodynamic relationship defining the spreading coefficient of liquid on solid as $S_{L/S} = \gamma_s - \gamma_L - \gamma_{SL}$ coincidentally happens to operate in a favorable direction? This point is mentioned simply to reemphasize the warnings of wiser minds than mine that experimentally determined surface constants can be subject to substantial errors primarily because of the large effects on surface energies of minute amounts of the ubiquitous oxygen. Bondi (15) is particularly outspoken on this point. Vanderslice (16) reports that even in the relatively excellent vacuum of 10^{-6} torr (1 torr = 1 mm Hg), pure, atomically clean metal surfaces become coated with a surface layer of gas within a few seconds. For pure, "clean surface" (i.e., gas-free) experiments, he prescribes pressures of at least 10^{-9} torr, where the time to contaminate a solid surface with gas is measured in hours. Thus, when applying exact thermodynamic relationships, the accuracy of the data used must be known.

Experimental Procedure. Originally it was planned to prepare several types of brazing alloys for experimentation by adding alkali and alkali-earth metals to various commercial silver base brazing alloys. These alloys were to have been rolled into strips and used as inserts in standard Navy bronze pipe fittings, (MIL-F-1183) from which sample joints were to be made with mild steel, 90-10 CuNi, 70-30 CuNi, and monel tubing. Brazing was to have been effected in the atmosphere using a reducing oxy-acetylene flame, and depending on this reducing flame atmosphere plus the confinement of the alloy within the joint to protect the reactive additive metal content during brazing.

It developed that preparation of alloys with alkali and alkali-earth metal content is no simple task, especially when the molten alloy is to be cast into 1/4 inch round billets for further cold reduction by swaging. A vacuum melting and casting technique was evolved and used which produced satisfactory results for the alkali-earths in silver-copper eutectic. Exact compositions are practically impossible to obtain. The reactive element oxidizes as it is beint cut and weighed. Then some of it vaporizes in the vacuum chamber and some of it reacts with the graphite crucible to form carbides, M_2C .

The combination melting - casting crucible is shown in figure (5). The charge, about 30 grams total per melt, was placed in the melting cap which was then pushed snugly into the mold cylinder. This assembly was placed melting-cap-down into a quartz tube, the tube was connected to a vacuum pump and evacuated for ten minutes, and then the lower half of the tube was



mold
cylinder

melting
cap

Figure (5). Combination melting-casting crucible.

inserted into a furnace preheated to 1000°C . When equilibrium temperature had been attained, the tube was quickly removed from the furnace and inverted. A small diameter quartz tube inserted through the rubber stopper and connected to the vacuum line served to keep the mold cylinder in the hot zone of the large tube. Inverting the tube, then, caused the melt to pour into the mold cavity where it soon cooled, all the time in an evacuated environment. The billet was then removed from the mold by drilling its end slightly and using a machinist's "E-Z-Out" extractor. This scheme worked very well for the alkali-earths, but during the attempt to make sodium-bearing alloy, the sodium vaporized and coated most of the interior of the quartz tube which then cracked and crazed badly on cooling.

For simplicity, the copper-silver eutectic was chosen as the base alloy. The additive elements were nominally measured as 2 wt %. Barium, calcium and strontium alloys were prepared. The sodium alloy was considered to be of such doubtful composition that it was discarded. Qualitative wettability determinations were made by examining the results of the melting of small quantities of each sample alloy on a mild steel coupon. Small pieces of each brazing alloy were melted on AISI-1020 mild steel coupons cut from $3/4$ inch rounds and ground on 400 grit paper. The coupons, with small piece of brazing alloy resting on the ground surface, were individually loaded into a Vycor glass furnace tube which was then flushed with nitrogen obtained as the boil-off effluent from the vent tube of a closed and stoppered Dewar full of liquid nitrogen. After flushing with nitrogen for ten minutes,

a concentric furnace, preheated to 1000°C , was slipped over the coupon-containing section of the Vycor tube and the brazing alloy allowed to melt whereupon the furnace was immediately removed and the coupon allowed to cool in the nitrogen stream.

The results for the barium-bearing alloy were as predicted in Table 12, pages 444-448 of Bondi's very thorough paper (7) and in reference (1). For calcium, the results again were predictable from reference (1), i.e., there was little or no detectable improvement in wettability of the steel coupon over the (poor) wettability of the plain silver-copper eutectic. Strontium produced a moderately good improvement in wettability, with a contact angle θ of about 30° .

Conclusions.

1. The practical determination of the parameters that are used in the thermodynamic equations of the surface chemistry of metals is an extremely difficult task, often producing uncertain results.
2. The addition of lithium, barium and strontium to silver-copper eutectic improves its ability to wet steel, lithium evidently effects the greatest improvement over plain eutectic Ag-Cu.
3. Because of the improvement in wettability, it is possible that lithium or barium additions to standard brazing alloys might measurably improve their performance in industrial applications. Further experimentation in this direction is indicated.

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